

Effects of Cloisite 20A Dispersion on the Structure and Properties of LDPE/Modified Clay/Coupling Agent Ternary Nanocomposites

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ABSTRACT: In this study, low-density polyethylene (LDPE)/modified clay (Cloisite 20A) nanocomposites were formed by melt-mixing Cloisite 20A with LDPE and coupling agent, low molecular weight oxidized polyethylene (OxPE). The effects of cloisite 20A, and OxPE on the morphological, mechanical, thermal and flame retardant properties of ternary nanocomposites based on LDPE were evaluated. The structural properties of nanocomposites were characterized with X-ray diffraction (XRD) and transmission electron microscopy (TEM). Mechanical, thermal and flame retardant properties were characterized by tensile test, differential scanning calorimetry (DSC), and flammable tests, respectively. The dispersion of cloisite 20A in LDPE depends on the amount of OxPE. When the amount of OxPE was 15 wt%, the exfoliated nanocomposite was achieved. Experimental outcomes confirmed that the addition of OxPE to LDPE/cloisite 20A increased tensile strength and tensile modulus but the elongation at break was less than that of LDPE. Cloisite 20A and OxPE addition did influence the melting/crystallization behavior of the nanocomposites. Significant improvements in flame retardant properties have been identified for ternary nanocomposite.

KEYWORDS: Low-density polyethylene, coupling agent, organoclay, mechanical properties, flame retardant properties

<https://doi.org/10.29294/IJASE.8.4.2022.2341-2349> ©2022 Mahendrapublications.com, All rights reserved

INTRODUCTION

Over the last few decades, the use of layered silicate nanoparticles, such as polymer-reinforced clay, has charmed much academic and industrial interest due to the expected improvement in properties. In nanotechnology, polymer nanocomposites consist of a polymer matrix filled with a layered silicate that is dispersed at a nanoscale phase. When the elements are well-defined by their size, at least one of the three external dimensions is about 1 nm to 100 nm [1]. Hybrid ingredients are formed by adding inorganic nanoparticles to the organic polymer matrix to form a class of polymer/clay nanocomposites. Generally, natural clay polymers are used as cheap raw components to manufacture nanocomposites due to their structure and availability. Inorganic nanoclay, which is commonly used, is montmorillonite, which has an aluminosilicate structure, with two tetrahedral silica sheets containing an octahedral alumina sheet. Polymer/clay nanocomposites

exhibit higher mechanical properties [2-4], compressive gas permeability, increased solvent resistance, high thermal distortion temperature (HDT), and increased flame retardant properties [5-8] than virgin polymer. Improved properties, including many exfoliated clay dispersing polar groups, are achieved by allowing the clay to easily disperse into such polymer matrix [9], while some studies of nonpolar polymers, such as polyolefin (PP or PE) have found a lower degree of clay exfoliation in the polymer matrix due to their hydrophilicity and poor interaction with the polar aluminosilicate surface of the clay [10].

Nanocomposite materials have gained important industrial interest and research endeavors to inspire the improvement of nanocomposite as well as other polymers. There are three ways to synthesize polyolefin/clay nanocomposites, namely situ polymerization, solution method, and melt compounding method. From all of these, the melt compounding method

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Received: 15.03.2022

Accepted: 17.04.2022

Published on: 18.05.2022

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is the simplest and most cost-effective way to manufacture nanocomposites. Polyethylene/organoclay nanocomposites are interested in the melt compounding process [11, 12]. Therefore, molten compounds are useful and safe for industrial purposes. Hence, it would be favorable for the industry to improve a strategy for making polymer/clay nanocomposite by melt compounding. Zhang et al. [13] reported that the flammability properties of polyethylene-clay nanocomposites have a significant reduction in peak release rate and also observed that polyethylene-clay nanocomposites have a mixed immiscible-intercalated structure. Natural montmorillonite, however, is hydrophilic so it is not compatible with many hydrophobic engineering polymers, as most polymer-layered silicates do not disperse easily. To get over this problem, a simple cation exchange procedure is used to produce montmorillonite clay organophilic. Thus, interfacial interactions between the clay layer and the polyolefin matrix should be introduced to develop polymer nanocomposite with a modified polar groups called coupling agents or interfacial agents in nanocomposite structures [14]. Maleic anhydride grafted polyolefin is commonly used as a compatibilizer. Many experimental results have shown the preparation and physical properties of manufactured polypropylene nanocomposites of maleic anhydride grafted polypropylene [15, 16]. Polyethylene/organo-clays, on the other hand, are less exposed to nanocomposites due to their non-polar chain structure and lack of thermodynamic forces, which is a great challenge to achieve structure [17]. In less research, some authors have suggested that low molecular weight (LMW) reactive compounds can be successfully used as a coupling agent for polyethylene nanocomposites [18, 19]. They suggested that these functional oligomeric compounds could easily disperse into clay galleries and cause additional delamination because they have much greater mobility during nanocomposite processing than their high molecular weight. Literary data on the use of low molecular weight oxidized polythene (OxPE) as a coupling agent for polymer/clay nanocomposites are relatively rare. In this research, we used low molecular weight (LMW) OxPE as a coupling agent to manufacture LDPE/organoclay nanocomposite. OxPE is a modified, LMW polyethylene that has several functions, for example, mainly carboxylic acids, esters, and ketones. It was used as a processing aid in some polymer blends as a coupling agent and coating formula. OxPEs have also been used in polymer blends as coupling

agents. In the present study, the effects of coupling agent content and the clay dispersion on the morphological, mechanical, thermal, and flame retardant properties of LDPE/organoclay nanocomposite were investigated.

EXPERIMENTAL

Materials and Nanocomposite Preparations

Granules of low-density polyethylene (LDPE) (density = 0.918 g/cm³, MI = 3 g/10 min) (trade name: Cosmoplene) were supplied by the Polyolefin Company, Private Ltd., Singapore. Low molecular weight oxidized polyethylene (molecular weight, M_n : 2950; acid number: 30) provided by Honeywell (AC® 330) was used as a coupling agent. Commercial organoclay Cloisite 20A (C20A) supplied Southern Clay Products. C20A was produced by cation exchange with 0.95 meq/g of dimethyl-dehydrogenated tallow ammonium chloride in sodium montmorillonite (Cloisite Na⁺, with a CEC of 0.926 meq/g). Tallow proportional (50%) may be a composition of unsaturated n-alkyl groups with approximate compositions: 65% C18, 30% C16, and 5% C14; hydrogenated tallow has only 3% unsaturation. The polymer and organoclay were dried in an air-circulating oven at a constant weight of 80°C. Compositions of LDPE/organoclay nanocomposites are listed in Table 1.

Table 1 Polyethylene blends and its nanocomposites.

Sample code	LDPE (wt%)	OxPE (wt%)	Cloisite-20A (wt%)
LDPE	100	-	-
LC5	95	-	5
LC5O10	85	10	5
LC5O15	80	15	5
LC5O20	75	20	5

LDPE: Low-density polyethylene; OxPE: Low molecular weight oxidized polyethylene

Various methods (intercalation of the polymer, in-situ intercalative polymerization, melt intercalation, direct mixture of polymer and particulates, template synthesis, in-situ polymerization, and sol-gel process) have been developed for the preparation of polymer nanocomposites. In the melt intercalation method, the mixture of polymer and the layered host is statistically annealed or above the

softening point of the polymer below the shear. Expansion of the polymer chain from bulk polymer melts in the gallery between the host layers during the annealing process (Figure 1) [20, 21]. The nanocomposites were made by mixing LDPE/5 wt% organoclay (LC5) and LC5/OxPE with 10, 15, and 20 wt% of OxPE using melt compounding in a co-rotating twin-screw extruder (Brabender Plasticorder, model: PLE-331). During polymer and organoclay loading, the rotor speed and temperature were maintained at 30 rpm and 180°C, for 3 min, respectively, then gradually increased to 60 rpm. The general blending time was 10 min.

After blending, the mixture was poured into a mold and therefore the molten nanocomposites were obtained by a hot compression-molding machine. The mixture was pressed at 10 MPa during a hydraulic press (Carver Laboratory Press, USA, Model 3856) at 190°C for 10 min. After that, the nanocomposite sample containing steel plates was cooled to another press (Carver Laboratory Press, USA, Model 2518) operated at cooling condition. Films of 2 mm thickness were made and cut to standard sizes and shapes to test the mechanical properties.

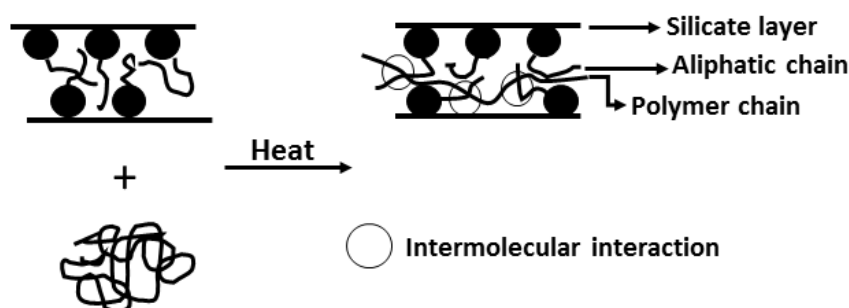


Figure 1. Melt intercalation synthesis of polymer/organoclay nanocomposite

Nanocomposite Test

The morphology of nanocomposites in LDPE/C20A has been observed using transmission electron microscopy (TEM: JEM 2010 F) with an acceleration voltage of 200 kV. A Sorvall MT6000 microtome was accustomed to cutting the skinny part (70 nm) of the specimen at room temperature.

The degree of intercalation or exfoliation was assessed with XRD. The XRD patterns were recorded employing a Philips X'pert MPD (40 kW, 30 mA) operating with Cu-K α radiation ($\lambda = 0.15406$ nm) at 40 kV and 30 mA within the range of $2\theta = 1-10^\circ$ with a scan speed of $0.02^\circ/\text{s}$. Interlayer spacing of the silicate layers was determined using the peak positions according to Bragg's law: $d = \lambda/(2\sin\theta)$, where λ is the wavelength, θ is the diffraction angle and d is the basal space between clay layers.

The tensile properties of virgin LDPE and LDPE/C20A nanocomposites were examined by tensile strength, tensile modulus, and elongation at break. Standard specimens were sampled from compression-molded sheets and

then conditioned at a temperature of $(25 \pm 2)^\circ\text{C}$ and relative humidity of $50 \pm 5\%$ for 24 h. To analyze the tensile properties of LDPE/C20A nanocomposites, the test was performed on a screw-driven universal testing machine (Instron-4466) equipped with 10 kN electronic load cells and mechanical grips at a crosshead speed of 30 mm/min according to ASTM standards. All values were measured 5 times to take the average value.

The thermal behavior of the specimens was analyzed by differential scanning calorimetry (DSC). Crystallization behavior of the specimens was performed on DSC-Mettler. In an aluminum crucible, a sample weighing about 5–8 mg was heated to 180°C from room temperature with a heating rate of $10^\circ\text{C}/\text{min}$ and kept at this temperature for 5 min to remove the thermal history. It was then cooled to room temperature with a cooling rate of $10^\circ\text{C}/\text{min}$ and reheated to 180°C with a heating rate of $5^\circ\text{C}/\text{min}$. All heating and cooling runs were conducted under a helium atmosphere at a flow rate of 25 ml/min. Melting peak temperature (T_m) and melting enthalpy (ΔH_m in J/g) were obtained from the second heat run. The degree of

crystallinity ($X_c\%$) was calculated using the melting enthalpy of the specimens in step with the subsequent equation:

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \quad (1)$$

where ΔH_m^0 is the melting enthalpy of the 100% crystalline form of PE (279 J/g) [22].

The flammability of virgin LDPE and nanocomposites was assessed by ascertaining their limiting oxygen index (LOI). Measurements were performed using FTA flammability equipment, supplied by Stanton Redcroft, by ASTM D-2863. The burn rate was set to LOI = 21.8 as the length of the plate which burns for one second.

RESULTS AND DISCUSSIONS

Organoclay Dispersion Analysis

It is well known that the dispersion of fillers in the polymer matrix can have a significant influence on the mechanical properties of the nanocomposite. Dispersion filler in thermoplastics isn't an easy process. The problem is even more severe, when using nanoparticles as filler because the nanoparticles have a strong tendency to agglomerate. Consequently, homogeneous dispersion of the nanoparticles in the thermoplastic matrix is a difficult process. A good dispersion can be achieved by adding a coupling agent such as OxPE. The dispersion of organoclay in LDPE nanocomposite was also confirmed by TEM monitoring. Figure 1(a-d) displays TEM micrographs of LDPE/C20A nanocomposites consisting of 5 wt% C20A (designated as LC5), LDPE/5 wt% C20A/10 wt% OxPE (denoted as LC5O10), LDPE/5 wt% C20A/15 wt% OxPE (marked as LC5O15), and LDPE/5 wt% C20A/20 wt% OxPE (abbreviated as LC5O20). Figure 1 (a) shows the dispersion of C20A particles in the LDPE matrix. It can be seen that most C20A particles form agglomerates in the LDPE matrix due to the incompatibility between nanoparticles and the LDPE matrix. The black shape represents the tactoids in C20A and the rest of the region represents an uninterrupted LDPE. Nevertheless, some black shapes may indicate some poorly dispersed C20A agglomerates. Figure 1 (b) on the other hand shows relatively fewer particles in C20A than in Figure 1(a) and the C20A particles were separated into lighter parts by the method of mixing. Anyway, image exfoliated structures

(white arrows) for LC5O15 (Figure 1 c) showed well-dispersed structures although several clay agglomerates and intercalated structures appeared simultaneously. Most C20A aggregates are broken down into primary particles. This should maximize the interfacial interaction between the C20A particles and the LDPE. This morphological monitoring by TEM was very consistent with other researchers [23]. However, both unexfoliated clay tactoid and exfoliated platelets are present in Figure 1(d). The LC5O20 sample has a large clay tactoid that corresponds to the intercalated structure. It can be clearly seen that the aspect ratio of clay layers in LC5O20 is higher than the aspect ratio of LC5O15. The stiffness of these probes can be attributed to the dispersion of silicate layers, which can determine the polymer phases which increase the stiffness which increases the stiffness [24]. These observations are supported by the results of the XRD analysis.

Dispersibility of Clay Layers in LDPE Matrix

The structure of polymer / clay nanocomposites is conventionally described using X-ray diffraction (XRD). Due to the periodic arrangement of silicate layers, XRD is the most widely used technique for identifying clay-intercalated structures. The XRD patterns of cloisite 20A (C20A), LDPE/5 wt%C20A (LC5), and LDPE/5 wt% C20A/15 wt% OxPE (LC5O15) nanocomposites are shown in Figure 2. Two diffraction peaks are observed for the 5 wt% C20A (C5) corresponding to basal spacing of $d_{001} = 2.96 \text{ nm}$ ($2\theta = 2.98^\circ$) and $d_{002} = 1.23 \text{ nm}$ ($2\theta = 7.17^\circ$) by using the Bragg equation. The d_{001} plane reflection of LC5 without coupling agent is observed at $2\theta = 2.80^\circ$ corresponds to $31.5\text{\AA}$ interlayer spacing. However, with adding OxPE, the peaks are shifted to lower angles in the nanocomposites. The d_{001} plane reflection of LC5O15 is observed at 2θ value of 2.37° , corresponding to $37.3\text{\AA}$ [25]. The peak height of the ternary nanocomposites (LC5O15) was very small, indicating an intercalated/exfoliated structure. This indicates the strong intercalation /exfoliation capacity of OxPE in the silicate layers. The driving force of the intercalation arises from the hydrogen bonding between the acidic carboxyl group of OxPE and the oxygen groups of silicates.

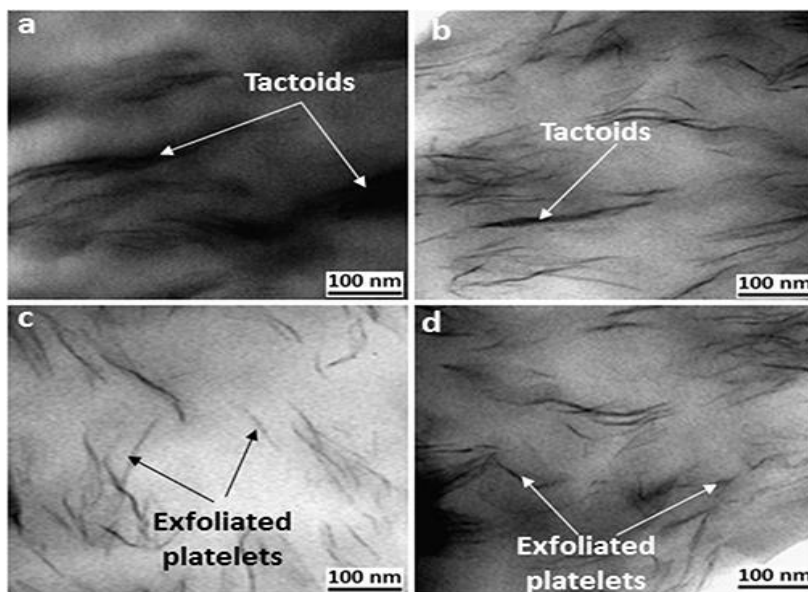


Figure 2 TEM images of nanocomposite samples: (a) LC5, (b) LC5O10, (c) LC5O15, and (d) LC5O20

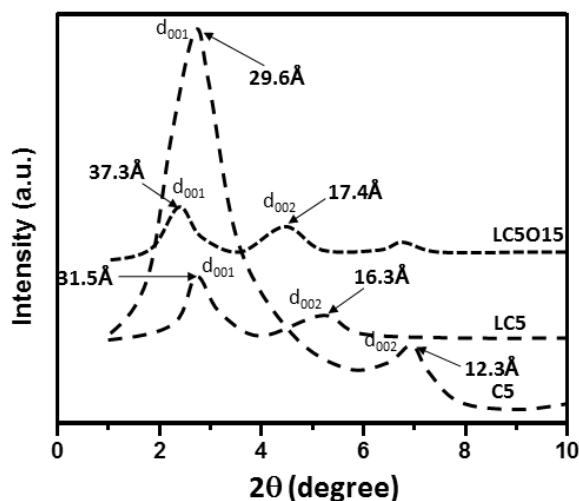


Figure 3 XRD patterns of 5 wt% C20A (C5), LDPE/5 wt%C20A (LC5), and LDPE/5 wt% C20A/15 wt% OxPE (LC5O15) nanocomposites

Tensile Properties of LDPE/organoclay Nanocomposites

The mechanical properties of nanocomposites are directly related to the homogeneous clay dispersion and exfoliation or intercalation of the polymer matrix. Interaction between exfoliated or intercalated nanoparticles and polymer matrix and large interfacial regions leading to high tensile strength, modulus, and thermal stability. More uniform clay dispersion may result in higher strength and modulus but at the expense of distortion and toughness such as elongation at breaks and impact resistance. The tensile properties of LDPE, LDPE/5 wt%C20A

(LC5), and LC5 nanocomposites with different coupling contents are illustrated in Figure 3. It was observed that when 5 wt % C20A (C5) was added to virgin LDPE, the tensile strength (TS) and tensile modulus (TM) of virgin LDPE increased with reduced elongation at break (Eb) and their value increased significantly as the OxPE content increased, but the Eb continuous declined. With C5 loading, the TS increased by about 22%, the TM enhanced by about 17%, and the Eb reduced by about 30% compared to virgin LDPE. The increased tensile properties can also lead to a rich interfacial bond between the matrix and C5 due to the C5 long aliphatic

chain leading to a rich interfacial bond between the matrix and C5. In general, the inclusion of organoclay in polymeric substances tends to reduce Eb. The results of Eb are illustrated in Figure 4. As seen in Figure 4, Eb of nanocomposites of the same C5 content followed this trend. Eb for nanocomposite samples decreased compared to LDPE. Typically, the filler causes a reduction in matrix deformation due to the role of the mechanical barrier [26].

The OxPE load reinforcing facility has been well observed in this investigation. It's interesting to determine how the OxPE was served in terms of the mechanical properties. The effect of OxPE load on the tensile properties of nanocomposites is shown in Figure 3. As can be seen in Figure 3, both TS and TM increased when adding OxPE with different content. OxPE nanocomposites exhibited a significant increase in TS compared to LC5 nanocomposites up to 15 wt% of OxPE loading and then decreased with increasing OxPE loading, while the TM of OxPE nanocomposites continuously increased up to 20 wt% of OxPE loading. The highest values obtained were 21.9 and 301 MPa, respectively, an increase of about 53% and 66% over virgin LDPE. Enhancement is achieved through strong hydrogen bonding between the -OH group of OxPE and the oxygen of silicate to the reinforcement of intercalated nanolayers, thereby increasing the inter-gallery space of the nanoclay [27]. At higher OxPE loads, the tensile test showed a decrease in nanocomposites due to lower exfoliation and dispersion of nanocomposites. The increased tensile performance of the OxPE mixture (when compared to the unmodified system) is sometimes explained by the fine dispersion generated by the OxPE and by an improved solid-state adherence, which ends up in stress transfer at the dispersion phase from the matrix. Considering the tensile test results of the samples, we have concluded that enhancement in mechanical properties not only originated from the state of organoclay dispersion but was also affected by the crystalline nature of the OxPE employed.

The TM of LDPE/5 wt% C20A/OxPE nanocomposites have improved dramatically with OxPE content. The increase in stiffness can be attributed to the dispersion of silicate layers, which can immobilize the polymer phases that stiffen the growth. In contrast, the tensile elongation at break of the LDPE/5 wt%

C20A/OxPE nanocomposites is reduced with OxPE content. This reduction in Eb of the nanocomposites as compared with the unfilled polymer is attributed to the fact that fillers generally decrease the ductility of polymers and similar trends are also seen for nanocomposites [28]. This suggests that the OxPE is effective in increasing adherence between C5 and LDPE molecular chains. A reduced Eb often means reduced energy to break. In short, better tensile properties were obtained due to better exfoliation and good dispersion of C5 in the LDPE matrix.

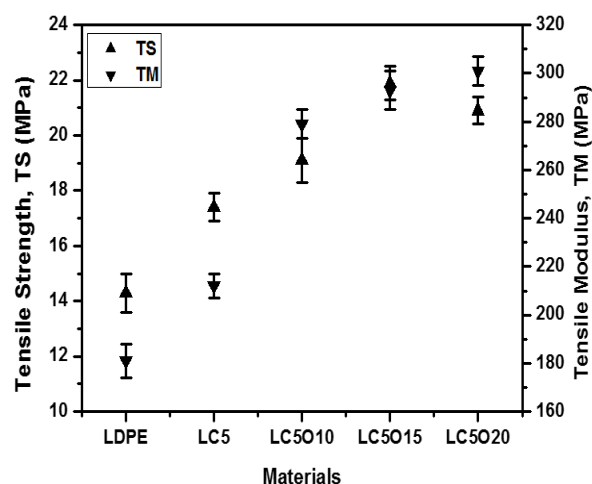


Figure 4 Tensile strength and modulus of virgin LDPE and its nanocomposites

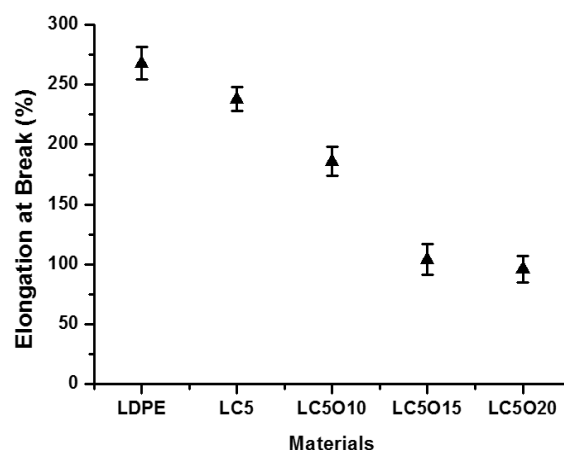


Figure 5 Elongation at break of virgin LDPE and its nanocomposites

Thermal Properties of Nanocomposites

Figure 5 (A) displays the crystallization exotherms of virgin LDPE, LC5, LC5O10, and LC5O15 nanocomposites recorded at a cooling rate of 10°/min during the cooling cycle. The crystallization, melting peak temperatures and degree of crystallinity are tabulated in Table 2.

This shows that the inclusion of organoclay and OxPE considerably changes the crystallization behavior of LDPE. As shown in Figure 5(A), the crystallization peak temperature (T_c) of the samples shifted to a higher temperature than the virgin LDPE, with increasing the content of the OxPE. The T_c increased from 95.7°C of LDPE to 99.8°C of C5 nanocomposite. For LC5010 sample, the T_c is increased up to 101.5°C. It's noteworthy that the T_c of the LC5015 sample increased to 102.9°C, much larger than the LDPE and even larger than the LC5010 nanocomposite. From Table 2, we can see that the melting peak temperature (T_m) has changed slightly with the increase in the content of the OxPE, and the T_m has increased slightly with increasing OxPE content. This is responsible for the heterogeneous crystallization on the organoclay surface, which can develop the crystallization of LDPE, slightly increasing the T_m of the nanocomposite [14].

The T_m of virgin LDPE, LC5, LC5010, LC5015, and LC5020 nanocomposites are in the range 109.6°C-111.4°C. Compared to virgin LDPE, the T_m of nanocomposites is transferred at higher temperatures and the maximum T_m is obtained at LC5015.

Figure 5 (B) displays the variation in X_c (%) of the specimens. Influenced by the introduction of OxPE content in the nanocomposites of LC5010, LC5015, and LC5020, X_c was higher than virgin LDPE. The inclusion of organoclay and OxPE contents into semicrystalline polymers increases the crystallization rate, resulting in higher crystallinity and higher T_c . According to Zaman et al [14], the inclusion of organoclay and OxPE to the LDPE matrix increases the crystallization percentage.

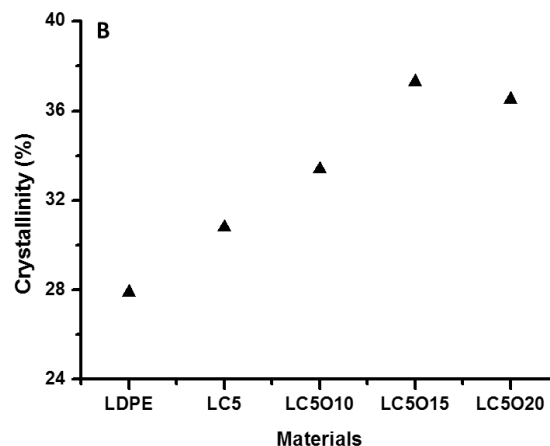
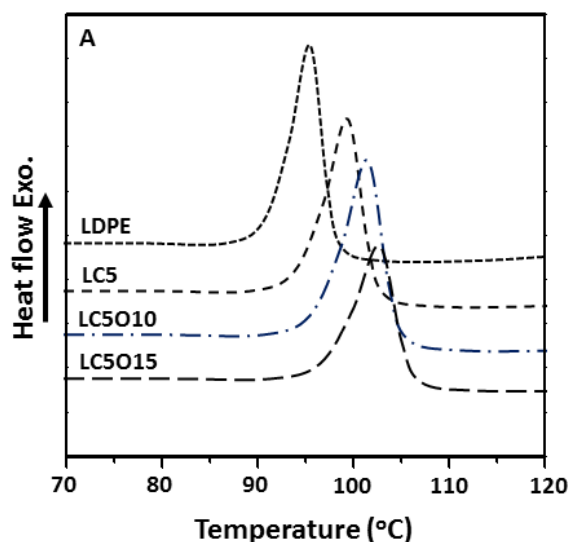


Figure 6. DSC (A) Crystallization exotherms and (B) crystallinity of virgin LDPE, LC5, LC5010, LC5015, and LC5020 nanocomposites.

Table 2. Thermal properties of virgin LDPE and its nanocomposites

Sample code	T_c (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)
LDPE	94.6	108.8	76.9	26.8
LC5	98.9	109.8	84.8	29.7
LC5010	100.8	110.7	92.4	32.8
LC5015	101.9	111.6	103.2	36.9
LC5020	101.7	111.4	101.5	36.6

Combustibility of the Nanocomposites

The limiting oxygen index (LOI) is measured by the volumetric fraction of O_2 within the N_2 mixture, where the substances still burn, are:

$$LOI = O_2 / (O_2 + N_2)$$

The higher the LOI of a given material, the lower its combustibility. The LOI value of the specimens is displayed in Figure 6 (a). It's worth noting that the virgin polymer LDPE has a relatively high LOI. The LOI values of binary nanocomposites are only LC5 higher than that of virgin polymer components. Therefore, the presence of organoclay reduces the combustion of the polymer. LOI increased with OxPE content increasing up to 15 wt% and then decreasing with increasing OxPE content. Furthermore, the presence of organoclay and the presence of OxPE lead to a significant reduction in the combustion rate of the substance up to 15 wt% (Figure 6 (b)). Nanocomposites exhibit burn retardant properties by creating a protective barrier to heat and mass transfer due to the accumulation of silicate and OxPE on the surface of the burning sample.

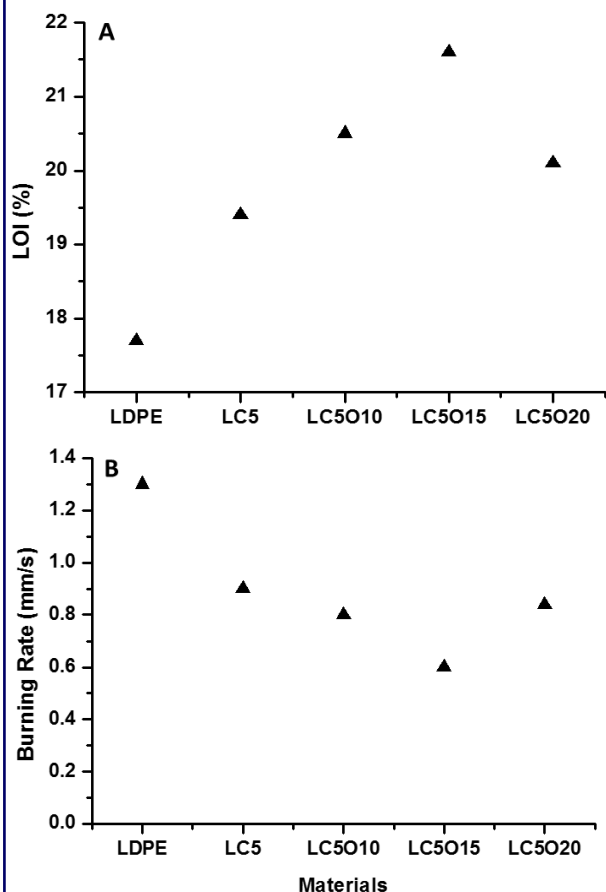


Figure 7 (A) Limiting oxygen index (LOI) of the virgin LDPE, LC5, LC5010, LC5015, and LC5020 nanocomposites; (B) Burning rate of the virgin LDPE, LC5, LC5010, LC5015, and LC5020 nanocomposites

CONCLUSION

In the present study, the tensile properties of LDPE/organoclay nanocomposites successfully manufactured by melt compounding method, using coupling agent (OxPE), were investigated. The characteristics of morphology, tensile properties, thermal behavior, and combustibility of LDPE/organoclay nanocomposites were examined by changing the inclusion of an OxPE. TEM photomicrographs exhibited that OxPE was effective in assisting the silicate platelet delamination. This outcome was also confirmed by the XRD of the specimens. The OxPE conferred higher tensile properties than control cases. DSC thermograms revealed that the crystallization temperature of the specimens increased significantly and the degree of crystallization in the nanocomposite increased with increasing OxPE concentration. However, melting and crystallization temperatures had a significant effect on blends and

nanocomposites. The results show that LC5015 nanocomposites have good flame retardant properties, which will be useful in terms of their application.

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